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A CO$_2$/N$_2$-Responsive Pickering Emulsion Stabilized by Novel Switchable Surface-Active Alumina Nanoparticles

An Chen [a,b], Duo Wang [b], Jingsi Chen [b], Jianhong Xu [a,*], Hongbo Zeng [b,*]

[a] State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
[b] Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB T6G 1H9, Canada

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ABSTRACT

This article reports the development of a novel switchable Pickering emulsion with rapid CO$_2$/N$_2$ responsiveness, which is stabilized using alumina nanoparticles hydrophobized *in situ* with a trace amount of a switchable superamphiphile via electrostatic interactions. With the introduction of CO$_2$ for 30 s, the Pickering emulsion can be spontaneously demulsified with complete phase separation; the emulsion can then be reconstructed in response to N$_2$ purging for 10 min followed by homogenization. Moreover, the stable Pickering emulsion can be stored for more than 60 days at room temperature without any visible change. The CO$_2$/N$_2$-responsive behavior of the switchable Pickering emulsion is attributed to the reversible desorption/adsorption of the switchable surfactants on the surfaces of the alumina nanoparticles upon the alternative bubbling of CO$_2$ or N$_2$. Thanks to the simple fabrication of the surfactant and the hydrophobization of the alumina nanoparticles, this research has developed an extremely facile and cost-efficient method for preparing a rapidly CO$_2$/N$_2$-responsive switchable Pickering emulsion. The dosage of the switchable surfactants has been significantly reduced by nearly 1500 times (from 150 to 0.1 mmol·L^{-1}) as compared with the dosage used in previous studies. Moreover, the as-prepared CO$_2$/N$_2$-responsive switchable Pickering emulsion is environmentally friendly, mild, and nontoxic; thus, it holds great potential for practical applications with considerable economic and environmental benefits, such as oil transport, fossil fuel production, environmental gases detection, and the encapsulation and release of active ingredients.

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1. Introduction

Switchable emulsions have been widely applied in a myriad of fields, such as drug delivery, oil transport, and fossil fuel production [1–3]. The preparation of a switchable surfactant is the key to switchable or stimuli-responsive emulsions, which can be reversibly transformed from surface-active forms to surface-inactive forms by means of certain triggers. To date, a variety of triggers have been employed for the fabrication of switchable emulsions, and their systems are mainly classified into two categories. Many systems can be switched by a single trigger, including pH [4–6], temperature [7,8], carbon dioxide/nitrogen (CO$_2$/N$_2$) [2,9–13], light irradiation [14,15], a magnetic field [16,17], and redox [18,19]. Other systems are dependent on multiple triggers, which can consist of magnetic field–temperature [20], pH–temperature [21,22], light–temperature [23,24], CO$_2$–light [25], and CO$_2$–redox [26] combinations. Compared with triggers based on the addition of acids, bases, oxidants, and reductants, which present inevitable economic and environmental issues, the use of gases such as CO$_2$/N$_2$ as triggers has attracted tremendous research interest over the last few decades because they are mild, nontoxic, cost-efficient, environmentally friendly, readily removable, and recyclable.

A CO$_2$/N$_2$-responsive switchable surfactant was first proposed in 2006 [9], where a long-chain alkyl amidine was synthesized to achieve a reversible transformation between emulsification and demulsification by means of a CO$_2$/N$_2$ trigger. The long-chain alkyl amidine was protonated by the addition of CO$_2$ to become charged amidinium in order to stabilize the emulsion. By purging N$_2$ into the emulsion to remove the CO$_2$, the charged amidinium was altered into the neutral form, resulting in a destabilized emulsion. In other works, a rapidly responsive superamphiphile was successfully applied to oil-in-water (O/W) emulsions to achieve CO$_2$/N$_2$-triggered switchable behaviors [11,13]. The superamphiphile was assembled by simply mixing two eco-friendly compounds through

* Corresponding authors.
 E-mail addresses: xujianhong@tsinghua.edu.cn (J. Xu), hongbo.zeng@ualberta.ca (H. Zeng).

noncovalent electrostatic interactions—unlike the amidine in the earlier work, which was synthesized via covalent bonds.

Emulsions stabilized by colloid particles (so-called Pickering emulsions) usually have better stability than emulsions stabilized by surfactants [27–31], as a dense particle film covers the oil/water interface to prevent the coalescence of droplets. The steric barriers between Pickering emulsion droplets are relatively difficult to destroy due to the high desorption energy of particles from the oil/water interface, making it a huge challenge to induce the demulsification of Pickering emulsions. However, in some industrial processes, the stability of an emulsion is only required temporarily and is followed by a controlled demulsification process, which has attracted great interest. Numerous attempts have been made to develop stimuli-responsive or switchable Pickering emulsions in recent years [6,10,21,32–38]. In general, the initially charged colloid particles are usually hydrophilic and surface-inactive in order to stabilize the emulsion; however, after the adsorption of oppositely charged switchable surfactants, the particles can be hydrophobized *in situ* to induce the formation of a Pickering emulsion, and the destabilization of the system can be realized by certain triggers. Jiang et al. [27] reported that negatively charged silica nanoparticles could be hydrophobized *in situ* through the adsorption of long-chain alkyl amidines via electrostatic interactions, resulting in the successful generation of a CO_2/N_2-responsive switchable Pickering emulsion. Nevertheless, the synthesis of long-chain alkyl amidines is relatively complicated, and the switching time is relatively long in comparison with some other CO_2/N_2-responsive surfactants.

In this work, we have developed a rapidly switchable Pickering emulsion stabilized by modified surface-active alumina nanoparticles, which display rapid responsiveness to CO_2 within 30 s to demulsify the stable Pickering emulsion; the emulsion can then be recovered back to its initial state through purging with N_2. The switchable surface-active alumina nanoparticles are developed by *in situ* hydrophobization through the adsorption of a trace amount of superamphiphile at the surfaces of the alumina nanoparticles, and the superamphiphile is prepared by a facile mixing of anionic fatty acid (oleic acid) and cationic amine (Jeffamine D-230) at a 1:1 molecular ratio. The switchable Pickering emulsion prepared using the hydrophobized alumina nanoparticles responds to gases rapidly and efficiently, as the stable Pickering emulsion undergoes a complete phase separation upon having CO_2 bubbled through it for 30 s, while the oil/water mixture can be re-emulsified to a stable Pickering emulsion by purging it with N_2 for 10 min. The adsorption behavior of the superamphiphile at the alumina nanoparticle surfaces has been well confirmed by measurements of zeta potential and interfacial tension. Furthermore, we have determined the switchable mechanism of the developed Pickering emulsions, which mainly occurs through the reversible desorption/adsorption of fatty acid molecules on the alumina nanoparticles upon alternatively bubbling CO_2 or N_2. Compared with the previously reported CO_2/N_2-responsive emulsions stabilized by superamphiphiles [11,12], the dosage of the switchable surfactant in this work is significantly reduced by nearly 1500 times (from 150 to 0.1 mmol·L^{-1}). The developed switchable Pickering emulsion is environmentally

friendly, with useful implications for practical applications such as oil transport, fossil fuel production, environmental gases detection, and the encapsulation and release of active ingredients.

2. Materials and methods

2.1. Materials

Hydrophilic alumina nanoparticles (Al_2O_3, > 99.8%) with a primary particle diameter of 13 nm and a specific surface area of 85–115 $m^2 \cdot g^{-1}$ (Brunauer–Emmett–Teller, BET) were purchased from Sigma-Aldrich, USA. Poly(propylene glycol) bis(2-aminopropyl ether) with an average molecular weight (M_w) of about 230 (Jeffamine D-230), which is a primary diamine with active amine groups, was purchased from Sigma-Aldrich, USA. Oleic acid (technical grade) was also purchased from Sigma-Aldrich, USA. Toluene (> 98%) was purchased from Fisher Scientific, Canada, and was used without purification as the oil phase for all emulsions. All the reagents were used as received. Deionized water (resistance ≥ 18.2 MΩ·cm) was obtained from a Milli-Q water purification system (Thermo Scientific, USA) and used in all the experiments. Unless specified otherwise, all experiments were carried out at room temperature.

2.2. Preparation of CO_2/N_2-responsive Pickering emulsion

Oleic acid and Jeffamine D-230 were mixed at a molecular ratio of 1:1, allowing the formation of a CO_2/N_2-responsive switchable superamphiphile—that is, a CO_2/N_2-responsive gemini-type amphiphile surfactant—through noncovalent electrostatic interactions (Fig. 1) [11]. The structure of the assembled superamphiphile was characterized by Fourier-transform infrared spectroscopy (FTIR) (Nicolet Is50, Thermo Scientific) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR, 400 MHz, $CDCl_3$); the results are shown in Figs. S1 and S2 in Appendix A. One of the amino groups of Jeffamine D-230 received a proton from the carboxyl group of oleic acid to transform into $-NH_3^+$, while the neutral carboxyl group was transformed into the ionized form ($-COO^-$), resulting in the bending vibration peak of $-NH_2$ shifting from 1586 to 1625 cm^{-1}, as shown in Fig. S1. The other amino group in the molecule was unreacted and existed at the other end of the superamphiphile; this was well confirmed by the vibrational peaks at 3362 and 3269 cm^{-1} in the high wavenumber regime, which were similar to those of the unprotonated amino groups in Jeffamine D-230. However, when different molar ratios of oleic acid and Jeffamine D-230 were mixed, the assembled superamphiphiles had different chemical structures. More details are provided in Refs. [11,12,39], and the FTIR and ^{1}H NMR spectra are provided in Figs. S1 and S2.

Superamphiphile solutions with different concentrations (0.1, 0.2, 0.3, 0.6, and 1.0 mmol·L^{-1}) were prepared by dissolving the surfactant in deionized water (resistance ≥ 18.2 MΩ·cm). A certain amount of alumina nanoparticles was weighed into a glass vessel; then, deionized water was added to the vessel to prepare the
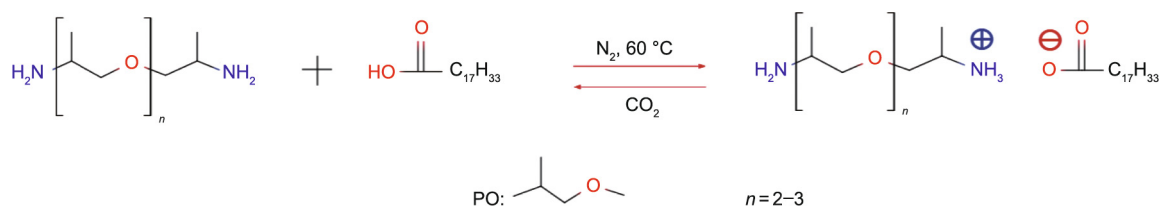

Fig. 1. Chemical structure and formation route of the CO_2/N_2-responsive superamphiphile.

alumina nanoparticle dispersions (0.1 wt%, 0.5 wt%, and 1.0 wt%). Solutions containing the superamphiphile and alumina nanoparticles were prepared by adding different volumes of surfactant solution (0.1, 0.2, 0.3, 0.6, and 1.0 mmol·L^{-1}) to the 0.5 wt% alumina nanoparticle suspensions, which were used as the aqueous phase for the preparation of Pickering emulsions. The superamphiphile and the alumina nanoparticles were dispersed using an ultrasonic probe (2510R-DTH, Marshall Scientific, USA) at an output of 100 W for 40 s. Three types of O/W emulsions in the presence of bare alumina nanoparticles alone, superamphiphile alone, and hydrophobized alumina nanoparticles with a trace amount of superamphiphile, were prepared by mixing 5.0 mL of the desired aqueous phase and 5.0 mL of toluene through homogenization in a 20 mL glass vial at room temperature (25 °C).

2.3. Interfacial tension measurement

The interfacial tension (IFT) between toluene and the aqueous superamphiphile solution in the absence or presence of alumina nanoparticles was characterized by means of the pendant drop method using a tensiometer (ramé-hart instrument co., USA) at room temperature. The aqueous solution, as the heavy phase, was loaded into a syringe with a straight needle, which was inserted in a sealed cell filled with toluene. A pendant droplet was generated at the tip of the needle by a syringe pump, with the volume remaining constant in each interfacial tension measurement. The droplet profile was captured by a high-speed charge-coupled device (CCD) camera every 1 s for 600 s. All the experiments were performed on an anti-vibration table. The aqueous phase used for the measurements included pure superamphiphile solutions with surfactant concentrations of 0, 0.1, 0.2, 0.3, 0.6, 1.0, 3.0, 6.0, 10.0, and 20.0 mmol·L^{-1}, as well as solutions containing 0.5 wt% alumina nanoparticles and superamphiphiles at concentrations of 0.1, 0.2, 0.3, 0.6, and 1.0 mmol·L^{-1}.

2.4. Zeta potential and particle size measurements

Alumina nanoparticles of 0.5 wt% were blended with superamphiphile solutions at different concentrations (0.1, 0.2, 0.3, 0.6, and 1.0 mmol·L^{-1}). The zeta potentials of the blended solutions, with or without introducing CO_2, were measured using a Zetasizer Nano ZSP (Malvern Instruments, UK). Dynamic light scattering was employed to monitor the size of the alumina nanoparticles in the solutions using the same instrument (Zetasizer Nano ZSP).

2.5. Switchable behavior of the Pickering O/W emulsion

The switchable behaviors of the prepared Pickering O/W emulsions were evaluated by alternatively introducing CO_2 or N_2. To be specific, the Pickering O/W emulsion was constantly bubbled with CO_2 at a flow rate of 300 mL·min^{-1} for 30 s, allowing the occurrence of demulsification. To re-stabilize the emulsion, the O/W mixture was stored in a water bath at 60 °C and purged with N_2 at a flow rate of 300 mL·min^{-1} for 10 min, followed by homogenization. Here, a faster flow rate resulted in a higher switching efficiency. However, a faster flow rate also had a certain negative impact on the actual operation, such as liquid splashing, energy consumption issues, and so on. Therefore, the specific operating conditions described in this work are the most suitable results, based on our continuous optimization. During the cycles of bubbling CO_2 and N_2, the pH values of the blended aqueous solutions were monitored. The stability of the Pickering emulsion was evaluated by visual observation and optical microscopy after being stored at room temperature for more than 60 days.

3. Results and discussion

3.1. Stabilization of Pickering emulsion by alumina nanoparticles and superamphiphile

Alumina nanoparticles are highly hydrophilic in deionized water and carry a positive charge, as is evident from the zeta potential measurement ((37.8 ± 0.5) mV) shown in Fig. 2(a). It is extremely difficult for bare alumina nanoparticles to completely disperse as single particles in an aqueous solution due to their high surface energy; thus, they usually form aggregates in aqueous solutions. In this work, the 0.5 wt% alumina nanoparticles usually formed aggregates with an average diameter of 182.3 nm in aqueous solutions (i.e., in deionized water at 25 °C), even though the suspension was sonicated using an ultrasonic probe, which is demonstrated by the size distribution shown in Fig. S3 in Appendix A. The toluene-in-water emulsions were prepared at different concentrations of alumina nanoparticles (0, 0.1 wt%, 0.5 wt%, and 1.0 wt%) followed by homogenization. However, separated phases were observed in all samples, implicating that the bare alumina nanoparticles alone were too hydrophilic to stabilize the O/W emulsion, as shown in Fig. S4 in Appendix A. Complete phase separation occurred rapidly, and most of the alumina nanoparticles sank into the aqueous phase due to their high density (3.95 g·m^{-3}) and hydrophilicity.

Toluene-in-water emulsions were also prepared using pure superamphiphile solutions at concentrations of 0.1, 0.2, 0.3, 0.6, and 1.0 mmol·L^{-1}, followed by homogenization. The O/W emulsions were stable for 24 h in the presence of a superamphiphile with a concentration greater than 0.3 mmol·L^{-1}, whereas separated layers were observed with a relatively long aging time (10 days) in all cases, as clearly shown in Fig. S5 in Appendix A. As shown in Fig. 2(b), even when the concentration was as high as 1.0 mmol·L^{-1}, the interfacial tension of the toluene/water interface still remained relatively high ($\sim$11.6 mN·m^{-1}), which suggested that it was not possible to form a long-term stable emulsion with a small amount of superamphiphile alone. This is why only high concentrations of superamphiphiles were used in previous studies to stabilize emulsions [11,12].

In contrast, the synergistic utilization of alumina nanoparticles and a superamphiphile dramatically promoted the stability of the O/W emulsions (Figs. 2(c)–(e)). After the O/W emulsions had been stored for 24 h, 10 days, and 60 days at room temperature, no obvious coalescence of oil droplets was observed, even though the superamphiphile concentration was down to 0.1 mmol·L^{-1}. This result indicated the excellent stability of the emulsions prepared with the combination of alumina nanoparticles and superamphiphile. As the bare alumina nanoparticles are hydrophilic and the pure superamphiphile cannot effectively reduce the interfacial tension, the enhanced stability can be attributed to the *in situ* hydrophobization of the alumina nanoparticles by the adsorption of the superamphiphile through electrostatic interactions, which was indicated by the change in the zeta potential of the alumina nanoparticles (Fig. 2(a)). The surfaces of the modified alumina nanoparticles were partially hydrophobic due to the formation of a surfactant monolayer, which stabilized the Pickering emulsion for a long time.

3.2. Switchable behavior of the CO_2/N_2-responsive Pickering emulsion

To demonstrate the switching property of the Pickering emulsion, a toluene-in-water (5.0 mL/5.0 mL) emulsion that was stabilized using 0.5 wt% alumina nanoparticles and a 0.3 mmol·L^{-1} CO_2/N_2-responsive superamphiphile was first prepared in a 20 mL glass bottle, followed by homogenization. The switchable behavior
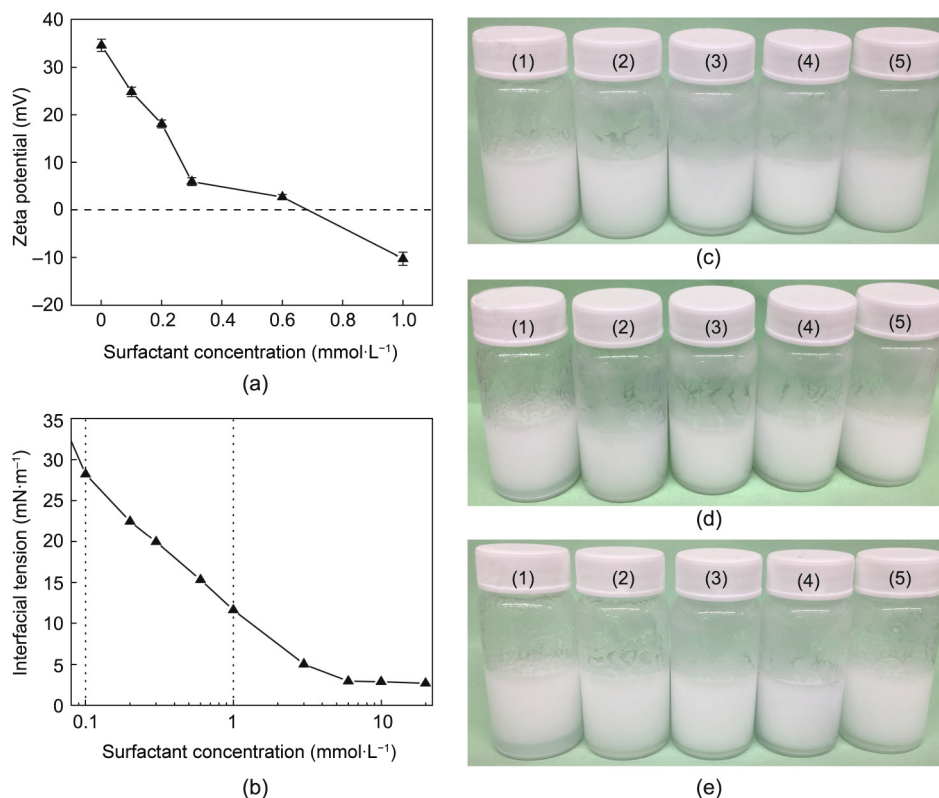
Fig. 2. (a) Zeta potentials of alumina nanoparticles dispersed in the surfactant solutions of different concentrations. The dotted line represents the boundary at which the zeta potential = 0. (b) Interfacial tension of the toluene/aqueous solutions as a function of surfactant concentration. The dashed lines represent the boundaries of surfactant concentrations of 0.1 and 1.0 mmol·L^{-1}. (c–e) Digital photographs of Pickering toluene/water emulsions (5.0 mL/5.0 mL) stabilized by alumina nanoparticles (0.5 wt%) and different concentrations of superamphiphile for an aging time of (c) 24 h, (d) 10 days, and (e) 60 days. The superamphiphile concentrations from (1) to (5) are 0.1, 0.2, 0.3, 0.6, and 1.0 mmol·L^{-1}, respectively.

of the resultant Pickering emulsion was investigated by alternatively bubbling CO_2 or N_2 for several cycles; the results are shown in Fig. 3. Without any treatment, the CO_2/N_2-responsive Pickering emulsion had a homogeneous appearance, and no visible signs of coalescence, demulsification, or phase separation occurred after aging the emulsion for 60 days, which demonstrated the superior stability of the Pickering emulsion (Fig. 3(f)). With the introduction of CO_2 at a flow rate of 300 mL·min^{-1} for 30 s at room temperature, the Pickering emulsion spontaneously demulsified and completely separated (Fig. 3(b)); reconstruction of the emulsion then occurred in response to N_2 purging at a flow rate of 300 mL·min^{-1} at 60 °C for 10 min, followed by homogenization (Fig. 3(c)). The results indicated that the switchable behavior (i.e., emulsification and demulsification) of the CO_2/N_2-responsive Pickering emulsion was highly sensitive and reversible upon alternately bubbling CO_2 or N_2. The reformed Pickering emulsion displayed similar droplet sizes to that before demulsification, as shown in Fig. 3(c′). Moreover, Figs. 3(d) and (e) highlight this switchable behavior in the second cycle, demonstrating the excellent repeatability of the proposed Pickering emulsion. If the surfactant could be properly replenished (as multiple introductions of gas consume the surfactant), then the maximum number of cycles could be higher.

During three cycles of alternatively bubbling CO_2 or N_2 into the Pickering emulsion, the pH value of the aqueous solution was monitored, as shown in Fig. 4. The original pH of the aqueous solution was 7.95, due to the adsorption of the ionized –COOH functional group (i.e., –COO–, the functional group of the superamphiphile) on the surface of the positively charged alumina nanoparticles. During the process of bubbling CO_2/N_2, the fluctuation of the peak of the pH value was extremely low (7.95, 8.11, 7.98, and 8.06 for

each peak), which may have been caused by an instrument measurement error. As CO_2 at a flow rate of 300 mL·min^{-1} for 30 s at room temperature was introduced into the Pickering emulsion, the dissolution of CO_2 resulted in a decrease in the pH to 4.83 and the protonation of carbonic acid. Moreover, the pH returned to the original value after bubbling with N_2 for 10 min at 60 °C at a flow rate of 300 mL·min^{-1} to remove CO_2. This finding indicated that the neutral superamphiphile transformed back to its active form for re-adsorption onto the surfaces of the alumina nanoparticles. These results fully demonstrated that the rapid responsiveness of the Pickering emulsion was provided by the switchable hydrophobization of the alumina nanoparticles, which could be modulated by the CO_2 trigger.

3.3. Switchable mechanism of the novel Pickering emulsion

Fig. 5 clearly shows that, without the addition of CO_2, the zeta potential of the prepared Pickering emulsion displayed a significant decrease with increasing superamphiphile concentration. In the initial state, the zeta potential of the positively charged alumina nanoparticles dispersed in pure water was around (37.8 ± 0.5) mV. It then decreased gradually as the surfactant concentration increased, indicating that the amount of negatively charged superamphiphile absorbed onto the surfaces of the alumina nanoparticles was increased. It was notable that the zeta potential value became negative when the superamphiphile concentration was greater than ∼0.7 mmol·L^{-1}, indicating that the modified alumina nanoparticles were negatively charged due to the adsorption of a large amount of active superamphiphile molecules. In contrast, when CO_2 was bubbled into the Pickering emulsion, the zeta
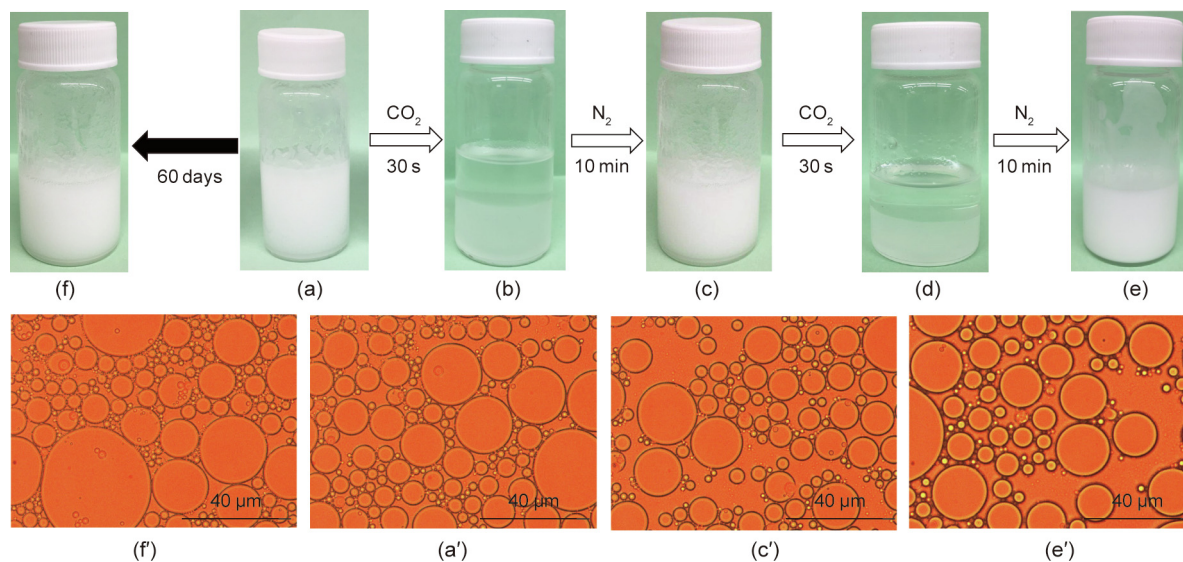
Fig. 3. (a–e) Appearance of the switchable Pickering emulsion stabilized by using 0.5 wt% alumina nanoparticles and 0.3 mmol·L^{-1} superamphiphile upon alternatively bubbling (b, d) CO_2 or (c, e) N_2 followed by homogenization. (f) Appearance of the Pickering emulsion after being stored for 60 days without any treatment. (a′, c′, e′, f′) Optical micrographs of droplet sizes of Pickering emulsion in (a), (c), (e), and (f), respectively.
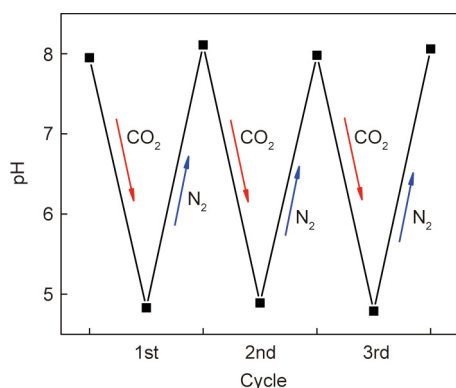

Fig. 4. Transient pH of the switchable Pickering emulsion for three cycles of alternatively bubbling CO_2 or N_2.

Fig. 5. Zeta potentials of alumina nanoparticles (0.5 wt%) dispersed in aqueous solutions of switchable surfactants, in both the active (ionic) and inactive (neutral) forms, as a function of surfactant concentration. The zeta potential alternation during cycles of bubbling CO_2/N_2 through the dispersion with 0.3 mmol·L^{-1} surfactant was as follows: point a: (5.9 ± 0.8) mV before CO_2 treatment; point b: (36.6 ± 0.7) mV in the presence of CO_2; point c: (5.9 ± 0.8) mV after N_2 treatment; point d: (36.6 ± 0.7) mV in the presence of CO_2 during the second cycle. These repeating values indicate that the absorption/desorption of the switchable surfactant from the solid/water interface took place following the alternative bubbling of N_2 or CO_2 through the solution, leading to reversible emulsification and demulsification.

potential remained positive at a constant value over the studied range of the superamphiphile concentration, indicating that the adsorption of neutral superamphiphile onto the surfaces of alumina nanoparticles was extremely low.

In order to investigate the CO_2/N_2-responsive behavior of the Pickering emulsions, samples were prepared with 0.5 wt% alumina nanoparticles and 0.3 mmol·L^{-1} superamphiphile; in this case, the zeta potential was determined to be (5.9 ± 0.8) mV (point a in Fig. 5) before CO_2 treatment and (36.6 ± 0.7) mV (point b) in the presence of CO_2. Furthermore, similar values (i.e., the overlapping points of a and c and of b and d in Fig. 5) were obtained in the second cycle of alternatively bubbling N_2 and CO_2, which indicated that the absorption/desorption of the switchable surfactant from the solid/water interface took place following the alternate bubbling of N_2 or CO_2 through the solution, leading to the emulsification/demulsification of the system.

The interfacial tensions of the as-prepared Pickering emulsions were investigated in order to unravel the emulsification and demulsification mechanisms, as displayed in Fig. 6. It is well accepted that the formation of surfactant-stabilized emulsions occurs due to a decrease in interfacial tension [40], which contributes to a lowered interfacial energy and enhanced stability of the O/W interface. In the presence of 1.0 mmol·L^{-1}
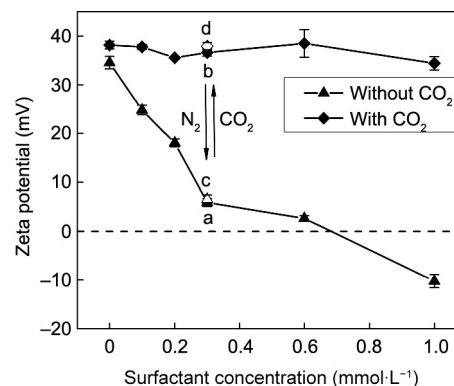
superamphiphile, the interfacial tension decreased from 32.5 mN·m^{-1} (without superamphiphile) to about 11.6 mN·m^{-1}. A negligible decrease of the interfacial tension was observed when the superamphiphile concentration was lower than 0.1 mmol·L^{-1}. This slight decrement of the interfacial tension is highly consistent with the results of the emulsification experiment (Fig. S5), in which a trace amount of superamphiphile could not stabilize the emulsions. On the other hand, Pickering emulsions with or without bubbling CO_2 exhibited profound stability in terms of interfacial intension with a superamphiphile concentration ranging from 0.1 to 1.0 mmol·L^{-1} (Fig. 6(b)); this was mainly due to the massive adsorption of active superamphiphile onto the surface of the alumina nanoparticles (without CO_2) and to the low interfacial activity and water solubility of the inactive superamphiphile [41] (with CO_2), respectively. These results reveal that the alumina nanoparticles were partially hydrophobized by the superamphiphile and
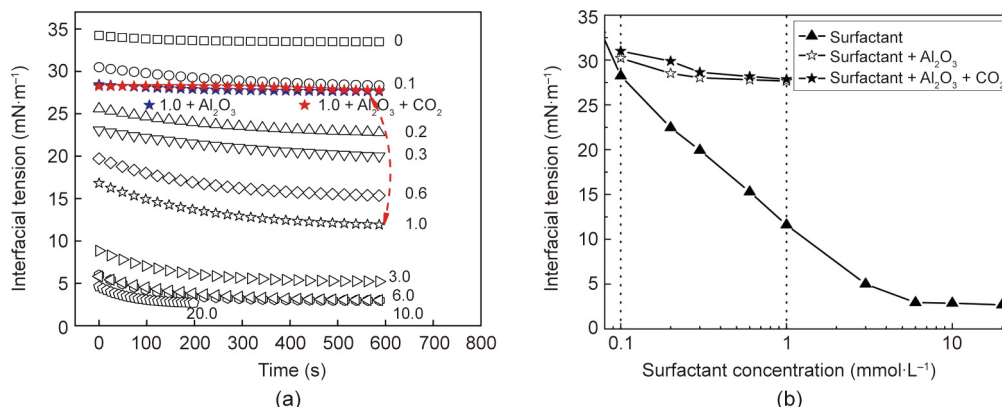
Fig. 6. Interfacial tension of toluene and aqueous solutions measured at 25 °C as a function of (a) time (the unit of the numbers is $mmol \cdot L^{-1}$) and (b) surfactant concentration after 30 min.

were then adsorbed at the oil/water interface, allowing the formation of a stable Pickering emulsion.

The switching mechanism of the CO_2/N_2-responsive Pickering emulsion is illustrated in Fig. 7. In an aqueous solution, the active superamphiphile is assembled through electrostatic interactions between the amino groups of Jeffamine D-230 (receiving a proton and transforming into $-NH_3^+$) and the carboxyl groups of oleic acid (transforming into the ionized form ($-COO^-$)). The positively charged alumina nanoparticles are hydrophobized *in situ* by the adsorption of active superamphiphile through electrostatic interactions, which was confirmed by the zeta potential results of the alumina nanoparticles and the results for the interfacial tension of the toluene/water interface. The surfaces of the alumina particles are covered with a surfactant monolayer with the hydrocarbon chains protruding toward the water, rendering a considerably stable Pickering emulsion. When CO_2 is introduced into the Pickering emulsion, the ionized carboxyl group of the superamphiphile is protonated by H^+ into a neutral form that is inactive, resulting in the desorption of the superamphiphile from the surface of the alumina nanoparticles. As neither the hydrophilic alumina nanoparticles nor the inactive superamphiphile molecules are capable of stabilizing emulsions, phase separation occurs as a consequence. With the removal of CO_2 upon purging with inert N_2, the reaction reverses back to the initial state, as the ionized carboxyl group is reformed and absorbed onto the surfaces of alumina nanoparticles, switching the separated phases to a stable Pickering emulsion.

4. Conclusions

In this work, CO_2/N_2-responsive Pickering emulsions were fabricated by employing alumina nanoparticles and a trace amount of synthesized superamphiphile, resulting in emulsions with rapid, highly efficient, and reversible switching characteristics. It was demonstrated that either hydrophilic alumina nanoparticles or a trace amount of superamphiphile are incapable of stabilizing emulsions on their own; however, when the alumina nanoparticles are hydrophobized with the ionized carboxyl group in the superamphiphile, they assemble into synergistic complexes and contribute to the high stability of the as-prepared Pickering emulsions. The switchable behavior of the Pickering emulsions in response to CO_2/N_2 was investigated, and it was demonstrated that the Pickering emulsions could rapidly, reversibly, and repeatedly switch from a stable status (in the initial state and after purging with N_2) to separated phases (when stimulated by CO_2). The underlying mechanism was studied by measuring the zeta potential, particle size, and interfacial tension; the results suggested that the reversible desorption/adsorption of the superamphiphile on the surfaces of the alumina nanoparticles upon alternatively bubbling with CO_2 or N_2 was responsible for the responsive behavior. It should be noted that only a trace amount of surfactant (0.1 $mmol \cdot L^{-1}$) is required to form a stable and switchable Pickering emulsion, as compared with the much higher dosages (e.g., typically ~150 $mmol \cdot L^{-1}$) that have been used in previous studies;
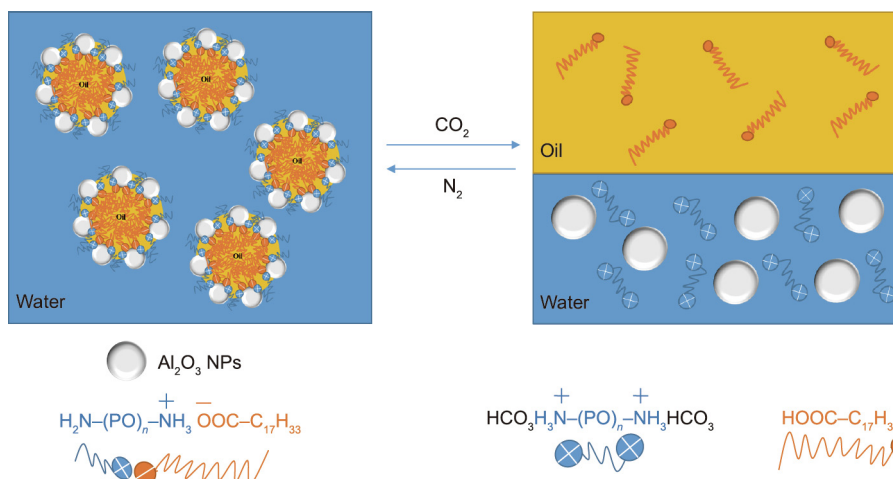

Fig. 7. Schematic diagram of the switching mechanism of the CO_2/N_2-responsive Pickering emulsion. NP: nanoparticle.

thus, the proposed method greatly reduces the dosage of surfactant by nearly 1500 times. Moreover, the as-prepared CO_2/N_2-responsive Pickering emulsion is environmentally friendly, mild, nontoxic, and cost-efficient. These results indicate that the novel CO_2/N_2-responsive Pickering emulsion holds great promise for many practical applications, such as oil transport, fossil fuel production, environmental gases detection, and the encapsulation and release of active ingredients.

Acknowledgments

Compliance with ethics guidelines

An Chen, Duo Wang, Jingsi Chen, Jianhong Xu, and Hongbo Zeng declare that they have no conflict of interest or financial conflicts to disclose.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eng.2020.08.031.

References

[1] Martínez-Palou R, Reyes J, Cerón-Camacho R, Ramírez-de-Santiago M, Villanueva D, Vallejo AA, et al. Study of the formation and breaking of extra-heavy-crude-oil-in-water emulsions—a proposed strategy for transporting extra heavy crude oils. Chem Eng Process 2015;98:112–22.

[2] Liang C, Harjani JR, Robert T, Rogel E, Kuehne D, Ovalles C, et al. Use of CO_2-triggered switchable surfactants for the stabilization of oil-in-water emulsions. Energy Fuels 2012;26(1):488–94.

[3] Li Y, Zhu L, Grishkewich N, Tam KC, Yuan J, Mao Z, et al. CO_2-responsive cellulose nanofibers aerogels for switchable oil–water separation. ACS Appl Mater Interfaces 2019;11(9):9367–73.

[4] Chu Z, Feng Y. pH-switchable wormlike micelles. Chem Commun 2010;46 (47):9028–30.

[5] Liu K, Jiang J, Cui Z, Binks BP. pH-responsive Pickering emulsions stabilized by silica nanoparticles in combination with a conventional zwitterionic surfactant. Langmuir 2017;33(9):2296–305.

[6] Yang H, Zhou T, Zhang W. A strategy for separating and recycling solid catalysts based on the pH-triggered Pickering-emulsion inversion. Angew Chem Int Ed Engl 2013;52(29):7455–9.

[7] Feng H, Verstappen NAL, Kuehne AJC, Sprakel J. Well-defined temperature-sensitive surfactants for controlled emulsion coalescence. Polym Chem 2013;4 (6):1842–7.

[8] Zhang W, Liu N, Zhang Q, Qu R, Liu Y, Li X, et al. Thermo-driven controllable emulsion separation by a polymer-decorated membrane with switchable wettability. Angew Chem Int Ed Engl 2018;57(20):5740–5.

[9] Liu Y, Jessop PG, Cunningham M, Eckert CA, Liotta CL. Switchable surfactants. Science 2006;313(5789):958–60.

[10] Jiang J, Ma Y, Cui Z, Binks BP. Pickering emulsions responsive to CO_2/N_2 and light dual stimuli at ambient temperature. Langmuir 2016;32(34):8668–75.

[11] Xu P, Wang Z, Xu Z, Hao J, Sun D. Highly effective emulsification/demulsification with a CO_2-switchable superamphiphile. J Colloid Interface Sci 2016;480:198–204.

[12] Chen X, Ma X, Yan C, Sun D, Yeung T, Xu Z. CO_2-responsive O/W microemulsions prepared using a switchable superamphiphile assembled by electrostatic interactions. J Colloid Interface Sci 2019;534:595–604.

[13] Wang Z, Ren G, Yang J, Xu Z, Sun D. CO_2-responsive aqueous foams stabilized by pseudogemini surfactants. J Colloid Interface Sci 2019;536:381–8.

[14] Khoukh S, Oda R, Labrot T, Perrin P, Tribet C. Light-responsive hydrophobic association of azobenzene-modified poly(acrylic acid) with neutral surfactants. Langmuir 2007;23(1):94–104.

[15] Takahashi Y, Fukuyasu K, Horiuchi T, Kondo Y, Stroeve P. Photoinduced demulsification of emulsions using a photoresponsive gemini surfactant. Langmuir 2014;30(1):41–7.

[16] Brown P, Bushmelev A, Butts CP, Cheng J, Eastoe J, Grillo I, et al. Magnetic control over liquid surface properties with responsive surfactants. Angew Chem Int Ed Engl 2012;51(10):2414–6.

[17] Yang H, Hou Q, Wang S, Guo D, Hu G, Xu Y, et al. Magnetic-responsive switchable emulsions based on Fe_3O_4@SiO_2–NH_2 nanoparticles. Chem Commun 2018;54(76):10679–82.

[18] Kong W, Guo S, Wu S, Liu X, Zhang Y. Redox-controllable interfacial properties of zwitterionic surfactant featuring selenium atoms. Langmuir 2016;32 (38):9846–53.

[19] Tsuchiya K, Orihara Y, Kondo Y, Yoshino N, Ohkubo T, Sakai H, et al. Control of viscoelasticity using redox reaction. J Am Chem Soc 2004;126(39):12282–3.

[20] Rahman MM, Chehimi MM, Fessi H, Elaissari A. Highly temperature responsive core–shell magnetic particles: synthesis, characterization and colloidal properties. J Colloid Interface Sci 2011;360(2):556–64.

[21] Tang J, Lee MFX, Zhang W, Zhao B, Berry RM, Tam KC. Dual responsive Pickering emulsion stabilized by poly[2-(dimethylamino)ethyl methacrylate] grafted cellulose nanocrystals. Biomacromolecules 2014;15(8):3052–60.

[22] Yi C, Liu N, Zheng J, Jiang J, Liu X. Dual-responsive poly(styrene-*alt*-maleic acid)-*graft*-poly(*N*-isopropyl acrylamide) micelles as switchable emulsifiers. J Colloid Interface Sci 2012;380(1):90–8.

[23] Fameau AL, Lam S, Velev OD. Multi-stimuli responsive foams combining particles and self-assembling fatty acids. Chem Sci 2013;4(10):3874–81.

[24] Jin Q, Liu G, Ji J. Micelles and reverse micelles with a photo and thermo double-responsive block copolymer. J Polym Sci A Polym Chem 2010;48(13):2855–61.

[25] Jiang J, Wang G, Ma Y, Cui Z, Binks BP. Smart worm-like micelles responsive to CO_2/N_2 and light dual stimuli. Soft Matter 2017;13(15):2727–32.

[26] Zhang Y, Guo S, Ren X, Liu X, Fang Y. CO_2 and redox dual responsive Pickering emulsion. Langmuir 2017;33(45):12973–81.

[27] Jiang J, Zhu Y, Cui Z, Binks BP. Switchable Pickering emulsions stabilized by silica nanoparticles hydrophobized *in situ* with a switchable surfactant. Angew Chem Int Ed Engl 2013;52(47):12373–6.

[28] Aveyard R, Binks BP, Clint JH. Emulsions stabilised solely by colloidal particles. Adv Colloid Interface Sci 2003;100–102:503–46.

[29] Chen D, Amstad E, Zhao CX, Cai L, Fan J, Chen Q, et al. Biocompatible amphiphilic hydrogel–solid dimer particles as colloidal surfactants. ACS Nano 2017;11(12):11978–85.

[30] Zhang M, Wang W, Xie R, Ju X, Liu Z, Jiang L, et al. Controllable microfluidic strategies for fabricating microparticles using emulsions as templates. Particuology 2016;24:18–31.

[31] Duan G, Haase MF, Stebe KJ, Lee D. One-step generation of salt-responsive polyelectrolyte microcapsules via surfactant-organized nanoscale interfacial complexation in emulsions (SO NICE). Langmuir 2018;34(3):847–53.

[32] Liang C, Liu Q, Xu Z. Surfactant-free switchable emulsions using CO_2-responsive particles. ACS Appl Mater Interfaces 2014;6(9):6898–904.

[33] Xu M, Jiang J, Pei X, Song B, Cui Z, Binks BP. Novel oil-in-water emulsions stabilised by ionic surfactant and similarly charged nanoparticles at very low concentrations. Angew Chem Int Ed Engl 2018;57(26):7738–42.

[34] Xu M, Zhang W, Pei X, Jiang J, Cui Z, Binks BP. CO_2/N_2 triggered switchable Pickering emulsions stabilized by alumina nanoparticles in combination with a conventional anionic surfactant. RSC Adv 2017;7(47):29742–51.

[35] Zhu Y, Jiang J, Liu K, Cui Z, Binks BP. Switchable Pickering emulsions stabilized by silica nanoparticles hydrophobized *in situ* with a conventional cationic surfactant. Langmuir 2015;31(11):3301–7.

[36] Ren G, Wang M, Wang L, Wang Z, Chen Q, Xu Z, et al. Dynamic covalent silica nanoparticles for pH-switchable Pickering emulsions. Langmuir 2018;34 (20):5798–806.

[37] Zhang Q, Bai RX, Guo T, Meng T. Switchable Pickering emulsions stabilized by awakened TiO_2 nanoparticle emulsifiers using UV/dark actuation. ACS Appl Mater Interfaces 2015;7(33):18240–6.

[38] Sarker M, Tomczak N, Lim S. Protein nanocage as a pH-switchable Pickering emulsifier. ACS Appl Mater Interfaces 2017;9(12):11193–201.

[39] Pudney PDA, Mutch KJ, Zhu S. Characterising the phase behaviour of stearic acid and its triethanolamine soap and acid–soap by infrared spectroscopy. Phys Chem Chem Phys 2009;11(25):5010–8.

[40] Rosen MJ, Kunjappu JT. Surfactants and interfacial phenomena. 4th ed. Hoboken: John Wiley & Sons; 2012.

[41] Chen Q, Wang L, Ren G, Liu Q, Xu Z, Sun D. A fatty acid solvent of switchable miscibility. J Colloid Interface Sci 2017;504:645–51.